Thermal Physics Notes

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Thermal Physics: PHYS 360

1 Introduction to the Course

- Why are we studying thermal physics?
- What is the relation between thermal physics and "regular mechanics" of particles and systems?
- What's the difference between statistical mechanics and thermodynamics?

Consider a baseball hit by a bat. We know how to model the ball as a point object and calculate its position $\mathbf{r}(\mathbf{t})$, its velocity $\mathbf{v}(\mathbf{t})$, etc. for all time t after it leaves the bat. What else is going on in the ball that we are not considering when we model it as a point particle and apply Newton's laws?

The ball consists of 10^{23} or so atoms bound into different molecules of different shapes and sizes all moving in "constrained randomness," that is, with a spectrum of velocities such that the center of mass motion tracks the position function $\mathbf{r}(\mathbf{t})$ that we know how to calculate. So, the ball has an additional reservoir of energy due to the motion of its constituent atoms and molecules. Are there other forms of energy present in the ball?

- chemical potential energies in molecular bonds,
- rest energies in atomic constituents,
- atomic energies in excited atoms, etc.
- ball radiates as a black body
- molecules in ball are exchanging energy with environment.

Some properties of the baseball are independent of the individual atomic identities and the quantum nature of atomic motion and interactions. These properties can be understood using the classical formulation of **Thermodynamics**. A detailed understanding of the baseball based on the quantum nature of its constituent atoms and molecules can be provided by the more fundamental formulation of **Statistical Mechanics**.

- Statistical Mechanics underlies thermodynamics.
- Statistical Mechanics is the logical foundation for Thermodynamics even though the latter was discovered first.

What is thermodynamics? the empirical science of relationships between bulk properties of matter

- 1. free energies, internal energies
- 2. pressure
- 3. entropy
- 4. enthalpy
- 5. heat capacities
- 6. chemical potentials

What is statistical mechanics?

- The application of probability theory to mechanics
- the formal relationship between microscopic properties and bulk properties of matter

• the logical foundation of thermodynamics

Taken together, let's call the topic of study **thermal physics**. Thermal physics is one of the most powerful and widely used formal constructs in all of science. The applications of thermal physics are diverse:

- high energy particle physics and cosmology
- protein folding
- atmospheric processes
- liquid/gas/solid phase studies
- solid state / quantum devices
- magnetism
- information theory
- neural networks

We will study thermodynamics first because its easier!

A complete understanding of the ball's motion is not possible without treating the ball thermodynamically. To see this, instead of a baseball, consider a rubber ball bouncing on the ground. Newton's second Law of motion describes the ball's motion and states that the net force acting on the ball is equal to the time rate of change of the ball's momentum:

$$F_{\text{net}} = \frac{d\vec{p}}{dt}$$

Is this a complete description of the possible behaviors of the ball? One problem we note right away is that N2 is time-reversal invariant. That is, replacing \vec{p} by $-\vec{p}$ and t by -t results in exactly the same motion and therefore the ball's motion should look the same whether we run time forward or backward. But a bouncing ball always comes to rest. Its motion does not look the same forward and backward in time.

So, the ball's motion is not entirely described by Newton's laws of motion alone. You might think that the addition of an energy conservation law is necessary here. Certainly, if we now say that the energy of the universe is conserved when the ball bounces, then it is easy to see that subsequent bounces of the ball will result in lower and lower heights as the ball "gives up" some of its energy to the air and the ground. So is the ball's motion completely described by energy conservation and Newton's laws?

Not quite. And this is where the second law of thermodynamics comes in. There is nothing about the conservation of energy that stipulates that the ball must always give up its energy to its surroundings. Why cannot the ball spontaneously *extract* energy from its surroundings, rising higher and higher with each bounce?

The answer is provided by the second law of thermodynamics and requires that something called the entropy of the universe must increase in every process or interaction. For now, think of entropy as a measure of the number of ways that energy can be distributed among the various "reservoirs" (air, ground, ball) such that the total energy remains conserved. The law of increasing entropy means that the energy must be ever more widely distributed in each bounce and with each interaction of atoms within the ball. This increasingly generous distribution of a finite amount of energy means that the ball itself has less and less available kinetic energy and so must bounce to lower and lower heights over time. Entropy is often referred to as "time's arrow" because of it's intrinsic role in breaking the time reversal symmetry of Newton's laws and conservation laws. Entropy defines the direction of time by insisting that all processes proceed along a one-way road of energy distribution.

2 Temperature and Thermal Equilibrium

Back to the baseball: As a result of collision with the bat, and possibly through interactions with the surrounding air molecules as it soars through the atmosphere, the ball heats up. *what does this mean microscopically?* What about after the ball has landed on the ground or in a player's mitt?

- After sufficiently long time, we say that the ball and ground have reached thermal equilibrium.
- Define temperature as the quantity that is the same when two objects are in thermal equilibrium.
- Define the <u>relaxation time</u> to be the time required to reach thermal equilibrium.

We can be more careful about our definition of temperature: Temperature:

- a measure of the tendency of an object to spontaneously give up energy to its surroundings
- a measure of the average kinetic energy per molecule in a substance

pes of equilibrium:	
Exchanged Quantity	Measure
Energy	T, V
Volume	V, P
particles	N
	Volume

Table 1: N=number of particles, V=volume occupied by particles, T=temperature, P=pressure

2.1 Temperature Scales

You will need to know how to quickly convert between different temperature measurement systems. You should already be familiar with the three common scales in use today. The Kelvin scale or the *absolute* temperature scale is "the most physical" in the sense that the unit of temperature (the Kelvin) is a standard SI unit in physics. The zero on the K-scale corresponds to the cessation of all motion. This is *absolute zero* and is a physically unrealizable state because to observe that an atom has no forms of kinetic energy associated with it requires a sufficiently powerful imaging device utilizing sufficiently short wavelengths of light with which to image the motion of the atom(s). These short wavelengths of light carry energy according to the Planck hypothesis $E = hc/\lambda$ which will give the atoms in question a little "kick" ensuring that one never sees absolutely no motion. Absolute zero is therefore unattainable. This is essentially a consequence of the <u>Uncertainty Principle</u>: The closer you look at the atom to make sure its not moving, the more energy you give it - ensuring that it is moving!

The unit size of the Kelvin scale is the same as that of the Celsius scale. Celsius was an astronomer and a contemporary of Fahrenheit, inventor of the mercury thermometer. While Fahrenheit was interested in establishing a scale based on internal human body temperature which he arbitrarily assigned to be 100 on his scale (later refined to be 98.6), Celsius was interested in rationally subdividing the temperature interval between the freezing and boiling of water at standard atmospheric pressure. Largely for the ease of instrument design, Celsius chose to subdivide the interval between freezing and boiling of water into 100 equal units, and determined that "0" should represent the freezing point of water, and "100" should represent the boiling point of water. Fahrenheit's scale has the freezing and boiling points at 32 and 212 respectively.

If the interval between 32 and 212 represents the same energy gain per molecule on the Fahrenheit scale as the interval between 0 and 100 on the Celsius scale, we can set up the following ratio:

$$\frac{\Delta T_F}{\Delta T_C} = \frac{212 - 32}{100 - 0} = \frac{180}{100} = \frac{9}{5} \tag{1}$$

Now, $\Delta T_X = T_X - T_X(initial)$, so we have $T_F - T_F(0) = \frac{9}{5}(T_C - T_C(0))$, or:

$$T_F = 32 + \frac{9}{5}T_C \tag{2}$$

Converting between the Kelvin and Celsius scale is even easier:

$$T_K = T_C + 273.15 \tag{3}$$

since absolute zero on the Kelvin scale is 273.15 °C below the zero on the Celsius scale. Question: Does it make sense to say that one object is twice as hot as another?

2.2 Thermal Expansion

This material should be familiar from previous courses in physics or chemistry. The microscopic picture here is that, when heated, the molecules in a piece of matter will acquire kinetic energy (except near a phase transition such as melting or boiling where the added energy goes into breaking molecular bonds). In many materials, this added kinetic energy endows the molecules with higher velocities that cause them to move apart from one another on average. So, as the material is heated, the molecules will be found on average further apart, and the material expands. The same thing occurs in reverse when the material is cooled. **There are important examples of materials that do the opposite: contract upon heating and expand upon cooling**. Can you think of some examples?

For a range of temperatures, this expansion is linear in the temperature difference. We recognize two empirical expressions of the thermal expansion of a substance:

1. For linear materials (rod, bar, or other quasi-one-dimensional object), the length of the thing grows according to

where α is called the coefficient of expansion and has units of inverse temperature, K^{-1} . α is a material property. That is, you look up its value in a table or measure it in lab for a given type of material. Example: a rod of length 1 meter is heated from 300 K to 400 K and is found to expand by 5.0 cm. What is the coefficient of expansion for this rod? Answer:

$$\alpha = \frac{\Delta L/L_0}{\Delta T} = \frac{0.05/1}{100K} = 5.0 \times 10^{-4} K^{-1} \tag{5}$$

Some typical values of α :

Table 2: Linear Coefficient of Expansion for Common Materials

Material	$\alpha(\times 10^{-6}C^{-1})$
Brass	19
Cu	17
Steel	12
Pyrex	3.3
Invar	0.9

Click Clack Consider a long (L = 1000 m) section of railroad track made of steel. The difference in temperature between a cold winter day and a hot summer day here can be around $\Delta T = 50^{\circ}C$. The change in length of this track from winter to summer will be

$$\Delta L = 12 \times 10^{-6} \times 10^3 \times 50 = 0.6 \text{m} = 60 \text{cm}$$

So, what will happen? The rail will bulge and buckle in the summer. Solution? Put gaps in the rail to allow expansion and contraction. To accommodate a 60 cm expansion over 1000 m, we can put 5 cm gaps at a spacing of 80 m on track. These are the source of the click-clack sound of a train speeding down the tracks.

2. For volumetric expansion of solids, a similar relation holds:

$$V = V_0 (1 + \beta \Delta T) \tag{6}$$

where β is the volume expansion coefficient. The thermometer problem in the homework requires you to apply this expression.

3 Ideal Gas Law

The ideal gas law is an example of an equation of state. That is, it is a relationship between *state variables* P, V, and T that collectively describe the state of a gas. We will derive this familiar relationship from first principles in chapter 3. For now, just recall it from your courses in physics and chemistry:

$$PV = nRT \tag{7}$$

or

$$PV = NkT \tag{8}$$

3.1 Moles and Avogadro's Number

The former is the "chemistry" expression of the IGL, while the latter is more commonly used in physics. To understand the distinction between the two forms, remember the definition of a mol: One mol of a substance contains Avogadro's Number of molecules (or atoms, or whatever else) of the substance.

- One mol of sand contains 6.02×10^{23} grains of sand.
- One mol of carbon contains 6.02×10^{23} atoms of carbon.
- n moles of hydrogen contains $n \times N_A$ hydrogen atoms.

3 IDEAL GAS LAW

Its typical to use n for the number of moles of a substance, N for the number of atoms or molecules, and $N_A = 6.02 \times 10^{23}$ to represent Avogadro's Number.

Example problems: How large of a box do you need to carry one mol of sand grains? Assume that the sand grains have an average diameter of 0.2mm (fine sand), and that the sand settles into a "close-packing" which means that the 74% of the available space is filled with sand and only 26% is taken up by "holes" in the packing.

With the given diameter, a typical sand grain occupies a volume of roughly 0.004 mm^3 . The total volume required is

$$\frac{N_A \times 0.004mm^3}{0.74} = 3.3 \times 10^{21} mm^3 \tag{9}$$

or a box with side length of around 9 miles!

A human body contains about 100 trillion cells (1×10^{14}) . There are around 6 billion people on the planet. So, the number of (living) human cells on the planet is roughly

$$10^{14} \times 6 \times 10^9 = 6 \times 10^{23} \tag{10}$$

There is about one mol of living human cells on the planet. Also, notice the relation implied by the two forms of the ideal gas law:

$$R/N_A = k \tag{11}$$

- R = 8.31 J/mol-K is referred to as the "Gas Constant."
- $k = 1.38 \times 10^{-23}$ J/K is "Boltzmann's Constant."

It is imperative that you memorize each of these constants and know their units and relationship.